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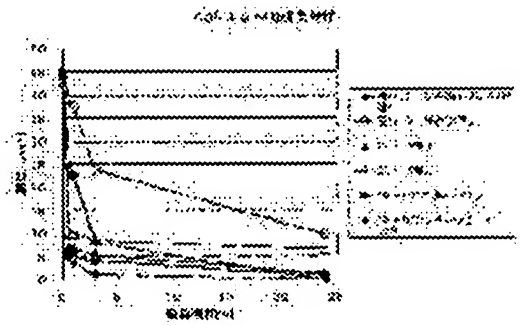
(54) FILTER MEDIUM AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a filter medium which has a deodorizing/decomposing effect of high persistence and exhibits the excellent deodorizing/decomposing effect to aldehyde-containing gas or ammonia-containing alkaline gas.

SOLUTION: The filter medium is manufactured by sintering a metal phthalocyanine compound on the surface of a silk-burned body which is obtained by burning/carbonizing a silk base stock and activating the burned/carbonized silk base stock to have many minute holes on the surface thereof.



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CLAIMS

[Claim(s)]
[Claim 1]
The filter material characterized by the metal phthalocyanine compound being sintered by the front face of the silk baking object with which the silk material was calcinated, and it carbonized, and was obtained, activation processing was further carried out, and many detailed holes were formed in the front face.
[Claim 2]
said silk baking object -- a nitrogen element -- less than [15wt%] -- the filter material according to claim 1 characterized by containing.
[Claim 3]
The process which acquires the silk baking object which calcinated the silk material and was carbonized,

The process which performs activation processing to the acquired silk baking object, and forms many detailed holes in the front face of a silk baking object,
The process which the silk baking object which performed activation processing is immersed [process] in a metal phthalocyanine solution, and makes a metal phthalocyanine compound adhere to a silk baking body surface,
The process which dries the silk baking object which adhered to the metal phthalocyanine compound,
The manufacture approach of the filter material characterized by including the process which heat-treats the dried silk baking object at the temperature of 300 degrees C - 400 degrees C under an inert gas ambient atmosphere or a vacuum ambient atmosphere.
[Claim 4]
The manufacture approach of the filter material according to claim 3 characterized by calcinating a silk material at the temperature of 1000 degrees C or less.
[Claim 5]
The manufacture approach of the filter material according to claim 3 or 4 characterized by immersing a silk baking object in a metal phthalocyanine solution for 30 minutes to 1 hour.
[Claim 6]
The manufacture approach of a filter material claim 3 characterized by making concentration of a metal phthalocyanine solution into 0.25 mmol/l - 1.00 mmol/l - given in 5 any 1 terms.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Field of the Invention]
[0001]
This invention relates to aldehyde system gas, and the filter material which is especially excellent in the deordorization decomposition effectiveness of ammonia system gas and its manufacture approach.
[Background of the Invention]
[0002]
A silk material is calcinated and carbonized, a silk baking object is acquired, subsequently to a silk baking object activation processing is performed, much pores are formed in a front face, and the filter material which made this silk baking object support a metal phthalocyanine compound is known further (international public presentation 2005 / 007287 pamphlet). A metal phthalocyanine compound absorbs various harmful matter, and since it decomposes, it is suitable as a filter.
[Patent reference 1] International public presentation 2005 / 007287 pamphlet
[Description of the Invention]
[Problem(s) to be Solved by the Invention]
[0003]
By the way, although the deordorization decomposition effectiveness improved in the above-mentioned filter material in various gas, such as a sulfur system (hydrogen sulfide), a methyl mercaptan compound, and an amine system, the technical problem which the deordorization effectiveness cannot say to be enough to aldehyde system gas and the alkaline gas of an ammonia system occurred. Moreover, the durability of the deordorization decomposition effectiveness was also inadequate.
Then, the durability of this invention of the deordorization decomposition effectiveness is high, and it aims at offering the filter material which is excellent in the deordorization decomposition effectiveness also to aldehyde system gas or the alkaline gas of an ammonia system, and its manufacture approach.
[Means for Solving the Problem]
[0004]
The filter material concerning this invention is characterized by the metal phthalocyanine compound being sintered by the front face of the silk baking object with which the silk material was calcinated, and it carbonized, and was obtained, activation processing was further carried out, and many detailed holes were formed in the front face.
said silk baking object -- a nitrogen element -- less than [15wt%] -- it is characterized by containing.
[0005]
Moreover, the manufacture approach of the filter material concerning this invention The process which acquires the silk baking object which calcinated the silk material and was carbonized, and the process which performs activation processing to the acquired silk baking object, and forms many detailed holes in the front face of a silk baking object, The process which the silk baking object which performed activation processing is immersed [process] in a metal phthalocyanine solution, and makes a metal phthalocyanine compound adhere to a silk baking body surface, It is characterized by including the process which dries the silk baking object which adhered to the metal phthalocyanine compound, and the process which heat-treats the dried silk baking object at the temperature of 300 degrees C - 400 degrees C under an inert gas ambient atmosphere or a vacuum ambient atmosphere.

[0006]
Moreover, it is characterized by calcinating a silk material at the temperature of 1000 degrees C or less.
Moreover, it is characterized by immersing a silk baking object in a metal phthalocyanine solution for 30 minutes to 1 hour.
Moreover, it is characterized by making concentration of a metal phthalocyanine solution into 0.25 mmol/l - 1.00 mmol/l.
[Effect of the Invention]
[0007]
According to the filter material concerning this invention, and its manufacture approach, the durability of the deordorization decomposition effectiveness is high, and can offer the filter material which is excellent in the deordorization decomposition effectiveness also to aldehyde system gas or the alkaline gas of an ammonia system.
[Best Mode of Carrying Out the Invention]
[0008]
The gestalt of operation of the filter material applied to this invention below and its manufacture approach is explained to a detail with reference to an accompanying drawing.
As mentioned above, the filter material concerning this invention is characterized by the metal phthalocyanine compound being sintered by the front face of the silk baking object with which the silk material was calcinated, and it carbonized, and was obtained, activation processing was further carried out, and many detailed holes were formed in the front face.
[0009]
Moreover, the manufacture approach of the filter material concerning this invention The process which acquires the silk baking object which calcinated the silk material and was carbonized, and the process which performs activation processing to the acquired silk baking object, and forms many detailed holes in the front face of a silk baking object, The process which the silk baking object which performed activation processing is immersed [process] in a metal phthalocyanine solution, and makes a metal phthalocyanine compound adhere to a silk baking body surface, The process which dries the silk baking object which adhered to the metal phthalocyanine compound, and the process which heat-treats the dried silk baking object at the temperature of 300 degrees C - 400 degrees C under an inert gas ambient atmosphere or a vacuum ambient atmosphere are included.
[0010]
A silk baking object is acquired by calcinating a silk material.
Silk materials are generic names, such as textiles which consist of a domestic silkworm or a wild silkworm, knitting, fine particles, cotton, and yarn, here. independent in these -- or it uses together and calcinates. If the textiles which make the shape of a sheet, and the silk material which consists of knitting are calcinated when using as a filter material, since it can use as it is, it is suitable.
[0011]
burning temperature -- 1000 degrees C or less -- especially -- 500 degrees C or less -- it is suitable if it calcinates at low temperature comparatively. Moreover, a firing environments is performed in inert gas, ambient atmospheres, such as nitrogen gas and argon gas, or a vacuum, and a silk material prevents burning and ashing. Also when calcinating in an inert gas ambient atmosphere, it is good to carry out under reduced pressure of 160Torr extent.
[0012]
Baking conditions are good to avoid rapid baking and to consider as loose conditions.
For example, in an inert gas ambient atmosphere, 100 degrees C [or less]/h, a temperature up is preferably carried out with the loose programming rate of 50 degrees C [or less]/h, and with this first burning temperature, the first burning temperature (for example, 500 degrees C) is held for several hours, and is calcinated the 1st order. Subsequently, once cooling even in ordinary temperature, to the second burning temperature (for example, 700 degrees C), too, a temperature up is preferably carried out with the loose programming rate of 50 degrees C or less, with this second burning temperature, it holds for several hours and the second bake of the 100 degrees C [or less]/h is carried out.
In addition, baking conditions are not limited above and can be suitably changed by the function of the class of silk material, and the silk baking object to search for etc.
[0013]

As mentioned above, carrying out a temperature up and calcinating with a loose programming rate, and by calcinating at the low temperature of 1000 degrees C or less, when the decomposition of the protein higher order structure in which amorphous structure and crystalline structure became intricate with about ten kinds of rapid amino acid was avoided and especially a nitrogen component remained so much, it was found out that various kinds of functions arise.
Moreover, by calcinating at low temperature 500 degrees C - 1000 degrees C or less, it does not graphite-ize but a flexible (there is flexible nature) silk baking object with black gloss is acquired.
[0014]
Drawing 1 is the Raman spectrum Fig. of the baking object at the time of calcinating a coarse-grain silk at a 2000-degree C elevated temperature. Having graphite-ized from a peak being seen at the place of 2681cm-1, 1570cm-1, and 1335cm-1 is understood.
[0015]
Drawing 2 , drawing 3 , and drawing 4 are the Raman spectrum Figs. of the baking object at the time of calcinating a coarse-grain silk at 700 degrees C, 1000 degrees C, and 1400 degrees C, respectively. Although peak value is low when it becomes the burning temperature of 1400 degrees C, the three above-mentioned peaks are seen. In the case of burning temperature 1000 degrees C or less, since the above-mentioned remarkable peak is not seen, it is thought that most graphite-ization has not taken place.
[0016]
Table 1 shows combustion and the melting type elemental-analysis result of the silk baking object which calcinated domestic silkworm silk at 500 degrees C. Many nitrogen components remain with 13.7wt (s)%. If it calcinates at about 400-degree C low temperature, a lot of about [15.0wt%] nitrogen components remain.
[Table 1]

元素	炭素（C）	窒素（N）	酸素（O）
w t %	69.8	13.7	8.4

[0017]
Table 2 shows combustion and the melting type elemental-analysis result of the silk baking object which calcinated domestic silkworm silk at 2000 degrees C. The amount of survival of a nitrogen component became zero.
[Table 2]

元素	炭素（C）	窒素（N）	酸素（O）
w t %	96.1	0.0	0.0

[0018]
Drawing 5 is a FE-SEM photograph Fig. at the time of calcinating a silk material at 700 degrees C. On a front face, thin film considered to be based on the baking residue of the amino acid origin, such as a nitrogen element, is seen.
On the other hand, although drawing 6 is an FE-SEM photograph Fig. at the time of calcinating a silk material at a 2000-degree C elevated temperature, a front face is beautiful and existence of the above film is not accepted.
[0019]
Table 3 shows combustion and the melting type elemental-analysis result of the object which carried out activation processing of the silk baking object which calcinated domestic silkworm silk at 500 degrees C with the 750-degree C steam. Moreover, Table 4 shows combustion and the melting type elemental-analysis result of the object which carried out activation processing of the silk baking object which calcinated domestic silkworm silk at 500 degrees C with the 850-degree C steam.
[Table 3]

元素	炭素（C）	窒素（N）	酸素（O）
wt%	80.3	8.3	6.1

[Table 4]

元素	炭素（C）	窒素（N）	酸素（O）
wt%	77.3	1.6	9.5

[0020]
Disappearance is not carried out, although a nitrogen component decreases when all carry out activation processing. a nitrogen component -- about 15wt% -- in that remaining makes deodorization property discover, although it is desirable, even if it is 1wt% of survival, deodorization property arises.
Thus, in order for a nitrogen component to remain, it is suitable to make burning temperature of a silk material into the temperature of 1000 degrees C or less as mentioned above.
In addition, activation processing of a silk baking object can be performed by exposing a silk baking object to a hot steam.
Or chemical activation, such as KOH, can also be performed. Or microwave processing may be carried out and activation of the silk baking object may be carried out again. This microwave processing is performed by irradiating microwave (frequency of 2.45GHz) for several minutes at a silk baking object. In case microwave is irradiated, in order to prevent a carbon material burning and ashing, it is good to put a carbon material by a porous sheet etc.
[0021]
The silk baking object acquired as mentioned above is made to support a metal phthalocyanine compound.
The support approach of this metal phthalocyanine compound can be performed at the usual process. That is, the silk baking object which carried out said pretreatment is immersed in a metal phthalocyanine solution, and a silk baking body surface is made to support a metal phthalocyanine compound.
Before supporting this metal phthalocyanine compound, adsorption of a stinking component and a decomposition (deordorization) function can be demonstrated more by carrying out activation processing of the silk baking body surface, forming irregularity in a front face, and increasing surface area. In addition, since the harmful matter adsorbed according to the supported catalyst is disassembled although most of that adsorption capacity force is no longer demonstrated when the amount of adsorption usually becomes saturation, it becomes possible to make it continue semipermanently of this adsorption function.
In addition, since the silk baking object which made the above-mentioned silk baking object and the metal phthalocyanine compound support has antibacterial and also disassembles various harmful matter, it is suitable as a filter material.
[0022]
When a metal phthalocyanine compound is made to support, a catalysis is demonstrated in ordinary temperature. Especially in the case of a metal phthalocyanine compound, it is suitable for disassembly of a sulfur system compound, and suitable for decomposition of methyl mercaptan, a hydrogen sulfide, disulfide, skatole, nicotine, an acetaldehyde, phenols, etc., and deodorization.
[0023]
In this invention, as mentioned above, after making a metal phthalocyanine compound support, the silk baking object which adhered to the metal phthalocyanine compound is dried, and, subsequently this dried silk baking object is heat-treated at the temperature of 300 degrees C - 400 degrees C under an inert gas ambient atmosphere or a vacuum ambient atmosphere.
[0024]
Thus, by heat-treating at the temperature of 300 degrees C - 400 degrees C, it sintered, where a metal phthalocyanine compound is distributed over the front face of a silk baking object at homogeneity (to

inside of pore), and the deodorization decomposition effectiveness continued for a long time by this, and it was checked aldehyde system gas and that the deodorization decomposition effectiveness of the alkaline gas of an ammonia system improves especially.

[0025]

In addition, if it heat-treats at a 300 degrees C - 400 degrees C elevated temperature in atmospheric air, a metal phthalocyanine compound will pyrolyze, but if it carries out under an inert gas ambient atmosphere or a vacuum ambient atmosphere, even if it is the above-mentioned hot heat-treatment, a metal phthalocyanine compound will not decompose. Moreover, since it can heat-treat at an elevated temperature more in this way, it is thought that sintering of a metal phthalocyanine compound is made good. The nitrogen content which remains on a silk baking object is also conjectured to contribute to firmer immobilization of a up to [the silk baking object of the metal phthalocyanine compound sintered when heat-treated by 300 degrees C - 400 degrees C].

[Example 1]

[0026]

The primary firing furnace was adjusted under reduced pressure of 160Torr(s), the temperature up of the silk material was carried out with the loose programming rate of about 50 degrees C/h to the first burning temperature (450 degrees C) in nitrogen-gas-atmosphere mind, it was held with this first burning temperature for 5 hours, and was calcinated the 1st order, and the silk baking object shown in drawing 5 was acquired.

When this silk baking object was exposed to the 850-degree C steam and activation processing was carried out, many minute holes (diameter of 0.1nm - about dozens of nm) were formed in the front face of a silk baking object, and the silk baking object with which surface area increased about [600-700m] to 2/g was acquired.

[0027]

1) Adjust the metal phthalocyanine solution (mixed solution of an iron phthalocyanine solution and a cobalt phthalocyanine solution) adjusted by the concentration width of face of 0.2 mmol/l - 1.00 mmol/l. The above-mentioned silk baking object was immersed by time amount width of face of 30 minutes - 24 hours, it was immersed for 10 minutes in the weak acidic water solution of an acetic acid, and this immersed sample was stirred in it, and was neutralized, stirring washing was carried out with distilled water for 30 more minutes to about 1 hour, subsequently it dried at 100 degrees C for about 1.5 hours, and the filter material was obtained. The sample of immersion time amount 30 minutes, 1 hour, 4 hours, 8 hours, and 24 hours is created, and the result of having investigated the hydrogen-sulfide deordorization property of this sample is shown in drawing 7 .

This test condition put in the sample in (the bottom of atmospheric pressure, temperature of 25 degrees C, 50% of humidity) the reaction container, it introduced the hydrogen sulfide so that it might be set to about 70 ppm, it measured the concentration of the residual hydrogen sulfide in a reaction container for every hour, and it measured it until concentration was set to 0 ppm. Drawing 7 shows that the thing of the sample of 30 minutes and 1 hour has [immersion time amount] the highest hydrogen-sulfide removal effectiveness.

In addition, when it was made into the above-mentioned concentration width of face, even if there was concentration of a metal phthalocyanine solution, the not much big difference in the removal effectiveness of a hydrogen sulfide was not seen. When it was bigger concentration than 1.00 mmol/l, the deordorization effectiveness decreased on the contrary. If concentration is too high, it will be considered to be the cause that a solution cannot permeate easily even in pore. Therefore, since the one where concentration is lower is advantageous even if it sees in cost, the above-mentioned density range is enough as the concentration of a metal phthalocyanine compound.

[0028]

2) Next, acid treatment neutralized the sample immersed in the metal phthalocyanine solution as mentioned above, the firing furnace performed the silk baking object dried under the 100-degree C ambient atmosphere with distilled water for about 1.5 hours for about 1 hour after stirring washing, heating sintering processing was performed under the inert gas ambient atmosphere for 1 hour - 2 hours at 300-degree-C or more temperature of 400 degrees C or less, and the sample of a filter material was obtained.

[0029]

Drawing 8 3) The sample which is not supported [of a metal phthalocyanine compound] (the sample to activation processing: sample 1), The sample which was made to support a metal phthalocyanine compound and was only dried (sample 2), A metal phthalocyanine compound is supported, after drying, as mentioned above, under an inert gas ambient atmosphere, a temperature up is carried out to 300 degrees C over 45 minutes, 300 degrees C is saved for 1 hour, and sintering and the hydrogen-sulfide deordorization property of the sample (sample 3) lowered and calcinated over 45 minutes are shown. CS shows a silk baking object among drawing. Moreover, a FeCo phthalocyanine shows the sample which supported both the iron phthalocyanine compound and the cobalt phthalocyanine compound. A test condition is the same as the case of drawing 7 . In addition, although the hydrogen sulfide carried out natural deodorization of the empty back within the container, he is data without putting in a sample. Even if it is the thing of the silk baking object of the sample 1 which does not support a metal phthalocyanine compound so that clearly from drawing 7 , as it is, the deordorization effectiveness of a hydrogen sulfide is high. Since the silk baking object itself has an alkaline property and this has a nitrogen functional group, it is guessed that it is what has the high deordorization effectiveness of the hydrogen sulfide which is a sour gas by this. As compared with the thing of a sample 1, as for the thing of the samples 2 and 3 which supported the metal phthalocyanine compound, the deordorization effectiveness of a hydrogen sulfide is high further. However, there was no difference so much at the thing of a sample 2 and the sample 3 further calcinated at the temperature of 300 degrees C. This is considered with since the silk baking object is excellent in the absorption property of a sour gas from the first.

[0030]

4) Drawing 9 shows the removal characteristic test data of formaldehyde gas. The test condition put in the sample in (the bottom of an atmospheric pressure, temperature of 25 degrees C, 50% of humidity) the reaction container, it introduced formaldehyde gas so that it might be set to about 45 ppm, and it measured the residual concentration of the formaldehyde gas in a reaction container every 1.5 hours till 24 hours. Although it compared with what only supported the metal phthalocyanine compound and heating sintering processing was carried out at the temperature of 300 more degrees C, the deordorization rate of direction of formaldehyde gas was clearly large.

[0031]

5) Drawing 10 shows the deordorization characteristic test data of ammonia gas. It is known that ammonia gas can be decomposed and deodorized also by irradiating ultraviolet rays. then, empty back + UV-irradiation, empty back + UV irradiation nothing, silk baking object (up to activation processing) + UV-irradiation, silk baking object (up to activation processing) + UV-irradiation nothing, and silk baking object (activation processing) + -- the ammonia gas deordorization property was only investigated with support of a metal (iron or cobalt) phthalocyanine compound, and the sample of heat treatment of +300 degrees C of silk baking object (activation processing) + metal (iron or cobalt) phthalocyanine compounds. The test condition put in the sample in (the bottom of atmospheric pressure, temperature of 25 degrees C, 50% of humidity) the reaction container, it introduced ammonia gas so that it might be set to about 45 ppm, and it measured the residual concentration of the formaldehyde in a reaction container every 1.5 hours till 24 hours. As shown in drawing 10 , it turns out that the thing of the sample of heat treatment of +300 degrees C (an iron phthalocyanine solution and cobalt phthalocyanine solution) of silk baking object (activation processing) + metal phthalocyanine compounds has the clearly quick deordorization rate of ammonia AGASU. Thus, by 300 degrees C - 400 degrees C heat treatment, a metal phthalocyanine compound is sintered by homogeneity in a silk baking body surface, and it is thought of with since it is fixed firmly that the deordorization effectiveness of alkaline gas becomes large. Moreover, since a metal phthalocyanine compound is fixed firmly, the deordorization effectiveness will be maintained at a long period of time. In addition, a lot of nitrogen content remains on the silk baking object as mentioned above, and it is surmised by a certain reaction of nitrogen content and a metal phthalocyanine compound again by performing 300 more degrees C - 400 degrees C heat treatment that a metal phthalocyanine compound is firmly fixed on a silk baking object.

In addition, in the above-mentioned example, although the iron phthalocyanine compound and the cobalt phthalocyanine compound were shown in the example, it is not restricted to this but it is checked that the effectiveness that other metal phthalocyanine compounds, such as copper, are almost equivalent is

acquired.
[Brief Description of the Drawings]
[0032]
[Drawing 1] It is the Raman spectrum Fig. of the baking object at the time of calcinating a coarse-grain silk at a 2000-degree C elevated temperature.
[Drawing 2] It is the Raman spectrum Fig. of the baking object at the time of calcinating a coarse-grain silk at a 700-degree C elevated temperature.
[Drawing 3] It is the Raman spectrum Fig. of the baking object at the time of calcinating a coarse-grain silk at a 1000-degree C elevated temperature.
[Drawing 4] It is the Raman spectrum Fig. of the baking object at the time of calcinating a coarse-grain silk at a 1400-degree C elevated temperature.
[Drawing 5] It is a FE-SEM photograph Fig. at the time of calcinating a silk material at 700 degrees C.
[Drawing 6] It is a FE-SEM photograph Fig. at the time of calcinating a silk material at 2000 degrees C.
[Drawing 7] The deordorization property of hydrogen-sulfide gas is shown.
[Drawing 8] The deordorization property of hydrogen-sulfide gas is shown.
[Drawing 9] The deordorization property of formaldehyde gas is shown.
[Drawing 10] The deordorization property of ammonia gas is shown.

[Translation done.]